

XXI. *On the Isolation of the Organo-Metals, Mercuric, Stannic, and Plumbic Ethyls; and Observations on some of their Derivatives.*—Second Memoir.

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SEVERAL years have elapsed since BUNSEN brought before the notice of chemists the interesting substance known as kakodyl. His elaborate memoir indicated, for the first time, the existence of a class of bodies now recognized as the organo-metals, the members of which, through the labours of FRANKLAND, LÖWIG, WÖHLER and others, have proved to be very numerous.

The series indeed ranges over a wide field, and on the one hand comprises organo-combinations with electro-negative metals, such as arsenic and antimony, and on the other hand embraces elements nearly allied to the noble metals, such as mercury and lead.

Mr. WANKLYN'S recent discovery of sodiummethyl shows also that the members of this class extend to the extreme limits of the electro-positive metals.

In a paper which the Royal Society has honoured me by publishing\*, I described some preliminary experiments, undertaken with reference to testing the analogies of some of the organo-metals containing mercury, lead, and tin. At the same time more than one method was shown by which their isolation could be effected. In the present memoir I have endeavoured to fill up the sketch then offered, and have added some considerations, supported by experiment, which it is hoped may prove of value in the interpretation of some of the more complex and less known individuals of the group.

*Mercuric Ethyl.*

*Action of Zincethyl on Iodide of Mercurous Ethyl.*—Although diffused daylight causes the decomposition of iodide of ethyl in presence of mercury, the action is slow, and requires many days' exposure before any considerable quantity of iodide of mercurous ethyl is formed. On this account attempts were made to obtain the salt by employing strong heat in sealed tubes.

The digestion was first made at a temperature of 130° C., and continued for four hours; but an examination proved that little or no change had taken place in the materials. The same tubes were afterwards heated for twelve hours from 160° to 170°, at the expiration of which time, much iodide of mercury had formed, in fine scarlet crystals. On cutting the tubes the internal pressure of gas was considerable, but no notable quantity of the required iodide was present.

\* Philosophical Transactions for 1858, p. 163.

From these experiments light would appear to be an almost necessary agent in the reaction.

It has been already shown that the radical mercuric methyl may be prepared through the reducing action of cyanide of potassium, the change being represented by the equation



The cyanogen principally occurs in the form of paracyanogen.

If the same process be adopted towards the corresponding ethyl compound, the quantity obtained is very trifling; almost the whole of the ethyl is disintegrated by the high temperature into gaseous products. A far more efficient and generally applicable method presented itself, from a consideration of the powerful and well-marked reactions of zincethyl on water, and on hydrochloric acid. There seemed to be well-grounded reasons for believing that interesting decompositions would result from the contact of zincethyl with various iodides and chlorides, of both the organo and true metals.

The radical mercuric ethyl may be very conveniently formed by introducing zincethyl into a retort, into which a slow stream of coal-gas is driven through the beak. Dry and powdered iodide of mercurous ethyl is then added, in small quantities at a time, through the neck, and incorporated by stirring. As soon as the zincethyl is saturated, which may be known by the stirring rod moistened with it ceasing to fume on exposure to the air, distillation may be commenced, and continued until gases alone pass over.

The product consists of a heavy liquid, mixed generally with a little ether. It is well again to distil with a slight excess of zincethyl, so as to ensure entire decomposition of the iodide. If this be neglected, the purification of the radical by rectification will be almost impossible.

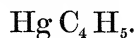
The distillate should be washed with dilute hydrochloric acid, to remove oxide of zinc, and afterwards well agitated with water. After the ether has been removed by rectification, a liquid remains which possesses a boiling-point between  $158^\circ$  and  $160^\circ$  C.

A portion thus prepared was analysed, and gave the following composition:—

I. 0.5305 grm., burnt with oxide of copper, gave 0.3630 grm. carbonic acid and 0.1780 grm. water.

II. 1.0457 grm., burnt with oxide of copper, gave 0.8078 grm. mercury.

These numbers very closely point to the formula



On comparing experiment with theory, we have in 100 parts—

	Theory.		Experiment.
1 equiv. of Mercury . . . .	100	77.53	77.24
4 equivs. of Carbon . . . .	24	18.60	18.66
5 equivs. of Hydrogen . . . .	5	3.87	3.72
	129	100.00	

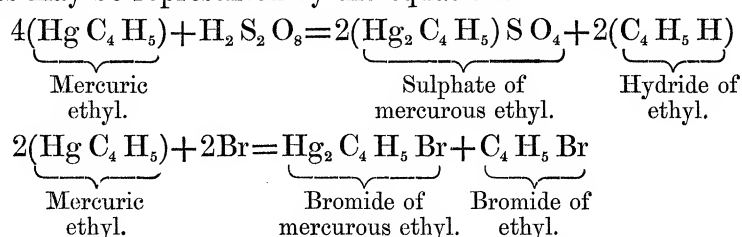
Mercuric ethyl is a perfectly colourless liquid, as limpid as water, and possessed of a

faint ethereal odour. Its specific gravity is 2.46. It burns with a smoky flame, more luminous than that of mercuric methyl, and disengages at the same time much mercurial vapour. It is very insoluble in water, less so in alcohol, but readily soluble in ether.

Towards concentrated sulphuric and hydrochloric acids, mercuric ethyl follows the deportment of its homologue, mercuric methyl. When the action is assisted by a gentle heat, hydride of ethyl is disengaged, and the crystalline sulphate or chloride of mercurous ethyl is produced in colourless plates. The radical bursts into spontaneous ignition when poured into a jar of chlorine gas, and the mercury is principally converted into chloride. With bromine and iodine also the action is violent; but if the action be conducted under water, ethyl gas or its products of decomposition are eliminated.

With a freezing mixture to moderate the reaction, the nascent ethyl gas unites with excess of bromine; and by distillation, bromide of ethyl may be obtained.

These changes may be represented by the equations—



If the vapour of mercuric ethyl be heated to about 226°, it is suddenly decomposed with a slight explosion, into mercury and an inflammable gas. This gas has not been analysed; but from reasons deduced from the behaviour of sodium towards this radical, there seems to be little doubt of its being a mixture of ethylene and hydride of ethyl, the results of a splitting up of a double molecule of ethyl.

From this tendency to decomposition at a high temperature, considerable difficulty was experienced in obtaining accurate numbers for the vapour-density of mercuric ethyl. In one experiment the apparatus was shattered by employing heat to fill the glass balloon with liquid, the mixture with air causing a loud detonation. This difficulty was easily overcome by inverting and dipping the mouth of the balloon in liquid, partially exhausting the air, and then causing the liquid to rise by atmospheric pressure. It is also necessary to draw the neck of the balloon very fine; otherwise the heat during sealing will infallibly cause a decomposition throughout the whole of the vapour.

	Grammes.	Pressure.	Temperature.
Weight of globe filled with vapour .	16.0895	767.60 mm.	194° C.
Weight of globe filled with air . .	15.3530	766.48 mm.	14° C.

$$P = 0.7365$$

$$\text{Capacity of the globe} = V = 118.75 \text{ cubic centimetres.}$$

$$\text{Volume of mercury entering the globe} = 117.25 \text{ cubic centimetres.}$$

$$\text{Difference} = v = 1.50$$

$$n_t = \text{weight of one cubic centimetre of air at } 14^\circ \text{ C.} = 0.001230.$$

$$n_v = \text{weight of one cubic centimetre of air at } 194^\circ \text{ C.} = 0.000755.$$

By placing these numerical values in MÜLLER'S formula, we have

$$\left. \begin{array}{l} \text{Specific gravity} \\ \text{of the vapour} \end{array} \right\} = \frac{P + Vn_t}{(V - v)n_t} = \frac{0.88256}{0.08852} = 9.97.$$

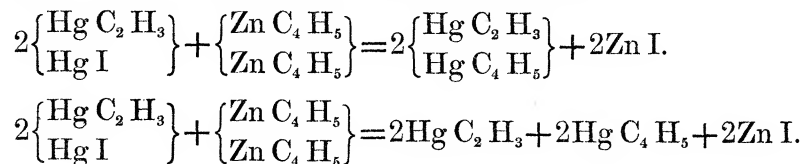
On dividing the equivalent weight, represented by the formula  $\text{Hg C}_4 \text{H}_5$ , by the experimental density, we obtain the number  $\frac{129}{9.97} = 12.94$ , which points sufficiently near to a condensation to two volumes. From the equivalent weight divided by the more accurate number 14.46, we find the theoretical density of mercuric ethyl to be  $\frac{129}{14.46} = 8.92$ .

The vapour-volume, therefore, coincides with that of zincethyl; and accordingly, to bring it into correspondence with four volumes, the formula should be doubled. If we consider the great difference in the two boiling-points of mercuric methyl, which equals  $96^\circ$ , and mercuric ethyl, which equals  $160^\circ$ , it appears more probable that the increment of  $64^\circ$  represents a greater difference in composition than is represented by one term,  $\text{C}_2 \text{H}_2$ .

Experiment perhaps has not yet satisfied this interesting question of the doubled formula. It was anticipated that a proof of its correctness would be shown by the reaction of zincethyl on iodide of mercurous methyl. The two bodies unite readily, and a rise in temperature indicates chemical action; but distillation of the product yields a liquid possessing no fixed boiling-point, the thermometer ranging between  $60^\circ$  and  $160^\circ \text{C}$ .

By fractional distillation a partial separation was effected into the two radicals, mercuric methyl and mercuric ethyl.

The anticipated and true decompositions were respectively,—



Notwithstanding the failure of proof in this experiment, the existence of a radical compounded of two molecules of mercury, one of methyl, and one of ethyl, cannot be considered as definitively settled in a negative.

#### *Action of Sodium on Mercuric Ethyl.*

The electro-negative character of the group  $\text{C}_{n2} \text{H}_{n2+1}$ , in the class of organo-metals to which zincethyl belongs, may now perhaps be considered as established; yet there would appear to be some importance in knowing the deportment of sodium towards ethyl, when combined with a metal like mercury. Mr. WANKLYN has shown how sodium, being more electro-positive than zinc, displaces that metal from zincethyl. If mercury should be positive to ethyl in a similar organo-metal, the sodium in like manner should displace the mercury and form sodiummethyl.

Sodium well freed from rock oil, was cut with clean surfaces, and introduced together

with mercuric ethyl into a glass tube. As scarcely any action was observed, the tube was sealed without heating the contents. After the lapse of five or six hours, a voluminous grey and spongy-looking mass was formed, which, from circumstances happening, was not immediately examined. The tube was left undisturbed in a cupboard for a week, at the expiration of which time, it suddenly burst and scattered the contents, which spontaneously ignited, and burnt so strongly, that some neighbouring woodwork was set on fire.

In another experiment one part of sodium was placed in a tube with five parts of mercuric ethyl. The mouth of the tube was drawn at the blowpipe into a capillary tube, the point of which was placed under a jar over mercury. If the temperature be low, gas is given off very slowly, and appears to cease when the grey sponge is formed. If, however, a gentle heat be applied, a powerful rush of gas is produced, which again slackens on cooling the apparatus. The first portion of gas was allowed to escape, as being mixed with atmospheric air. It did not fume, but gave a white flame when ignited. Bottles were filled with the gas both at the commencement and towards the close of the disengagement, when the action became more moderate. On a supposition that the gas might contain ethylene, portions were subjected, in a graduated tube, to fuming sulphuric acid, introduced by means of a coke ball. The acid fumes were afterwards removed by a ball of fused potash.

	First sample.		Second sample.
	I.	II.	III.
Corrected volume of gas . . . . .	74·14	74·24	73·24
After absorption by $\text{H SO}_4$ &c. . . . .	48·63	48·63	10·56
Volume of ethylene . . . . .	25·51	25·61	62·68
Gas transferred.			
Corrected volume . . . . .	45·19	42·23	
+Oxygen taken . . . . .	238·71	260·23	
+Air taken . . . . .	411·10	416·80	
After explosion . . . . .	292·60	308·10	
After absorption by KO . . . . .	206·38	225·98	
Total of oxygen taken . . . . .	229·66	250·80	
Total of oxygen burnt . . . . .	159·53	148·59	
Carbonic acid formed . . . . .	86·22	82·12	
One volume of gas therefore consumed	$\left. \begin{array}{l} 159\cdot53 \\ 45\cdot19 \end{array} \right\} = 3\cdot53 \text{ vols. of oxygen,}$		
in first experiment . . . . .			
and produced . . . . .	$\left\{ \begin{array}{l} 86\cdot22 \\ 45\cdot19 \end{array} \right\} = 1\cdot91 \text{ vol. of carbonic acid.}$		
One volume of gas also consumed in	$\left. \begin{array}{l} 148\cdot59 \\ 42\cdot23 \end{array} \right\} = 3\cdot51 \text{ vols. of oxygen,}$		
second experiment . . . . .			
and produced . . . . .	$\left\{ \begin{array}{l} 82\cdot12 \\ 42\cdot23 \end{array} \right\} = 1\cdot96 \text{ vol. of carbonic acid.}$		

These eudiometric results indicate that this gas must be either methyl or its isomer, hydride of ethyl, both of which satisfy the conditions of the above experiments. They may be distinguished, however, by their different behaviour towards chlorine gas. The gas under examination, when exposed to diffused daylight, absorbed a large quantity of chlorine, and after some hours crystals of sesquichloride of carbon made their appearance, thus affording a clear proof of the gas being hydride of ethyl.

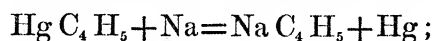
A comparison of the first and last samples of gas taken for analysis, shows that the ratio of the gases ethylene and hydride of ethyl is not constant at all phases of the experiment.

	First sample.		Second sample.
Ethylene . . . . .	0·655	0·654	0·856
Hydride of ethyl . . . .	0·345	0·346	0·144
1 volume . . . . .	1·000	1·000	1·000

No doubt these gases are produced by the decomposition of a double molecule of ethyl; yet from the circumstance that little or no gas is disengaged at ordinary temperatures after the spongy matter has been formed, it is probable that the grey body is a double compound with sodiummethyl, or at all events contains that body. All attempts to discover the real nature of this grey material have as yet failed. Its component parts are evidently in a very unstable condition of equilibrium; for the body is liable to explosion, and often without an assignable cause. In one experiment, a loud detonation followed the dropping of a few lumps of the substance into alcohol. On repeating the experiment, the entire contents of the tube, containing the grey matter, exploded violently, and, as it were, sympathetically, leaving behind scarcely a vestige of the glass. This phenomenon was perhaps caused by the detonation of that portion of the body which touched the alcohol, transmitting the shock through the air to the remainder.

The grey material loses its explosive properties after it has been cautiously, but rather strongly heated; yet even then, after it is cold, it becomes incandescent on freely admitting air to its surface.

From these experiments it is concluded that ethyl, and doubtless methyl, in these organo-metals is still negative to mercury, and therefore we should not suppose, with Mr. WANKLYN, that mercury, copper, and platinum would displace ethyl from sodium-ethyl. The foregoing reactions would rather tend to show that sodiummethyl is formed from sodium and mercuric ethyl, and it is only by heat that that body is broken up,



and by heat,

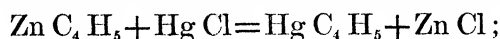


The mercury is not supposed to be active in the last decomposition, or in any way to determine it; but being present, it simply forms an amalgam with the liberated sodium.

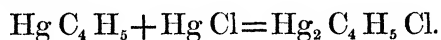
*Action of Zincethyl on Chloride of Mercury.*

Having thus effected the reduction of an organo-metallic salt through zincethyl, it was important to see how far an ordinary iodide or chloride would follow the same deportment. Corrosive sublimate produces much heat when mixed with zincethyl, so much so as to render it necessary to cool the retort by water or other means, to prevent waste of the zincethyl.

After breaking up the cake of chloride of zinc which is formed, the radical may be obtained in considerable quantity by distillation, and washing the product with dilute acid, as before described. Excess of mercuric chloride, however, must be carefully avoided, as chloride of mercurous ethyl would be produced according to the equations,



by addition of mercuric chloride,

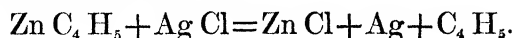


Although this process gives certain and good results, it will not be found so economical in practice as that previously noticed. Iodide of mercurous ethyl is readily made; and by its employment it is very obvious that a less consumption of zincethyl is required.

*Action of Zincethyl on Chlorides of Silver, Copper, and Platinum.*

Dry powdered chloride of silver strongly reacts on zincethyl, turning quite black and liberating much gas. The chloride, however, seems to be incapable of decomposing the whole of the zinc radical, even when in excess and heat is applied. The clear liquid was removed by a pipette and treated with water, which extracted simply chloride of zinc, and isolated no silver compound. The black matter in the retort contained a mixture of chloride and metallic silver.

In another experiment anhydrous ether was employed instead of water, under the supposition that a solid silver compound might be present, which was soluble in ether. The only reaction, however, seemed to be,



Results have also been negative with reference to the formation of radicals containing copper or platinum.

Protochloride of copper immediately loses its green colour on mixing with zincethyl, a circumstance very probably due to a loss of traces of water. No combination is effected; and on exposure to the air, the black powder speedily recovers its green hue.

Well-dried protochloride of platinum decomposes zincethyl into chloride of zinc and gaseous matter. The metal is reduced in the form of platinum black.

*Stannic Diethyl.*

Much of the uncertainty which attaches to the compounds styled by LÖWIG, in his laborious researches, "ethyl-stanethyl," "aceto-stanethyl," &c., is doubtless due to the

method he adopted for forming the iodides of stanethyl and stibethyl, from which salts all the bodies described by him appear to have been obtained.

The plan adopted in the present memoir has proceeded rather in an opposite direction,—the wish being, first to construct the pure radical, and then to form from it the various salts, according to the mode usually adopted in the case of an ordinary metal.

The iodide of stanethyl employed was prepared by Dr. FRANKLAND's process. Sealed tubes containing iodide of ethyl and excess of tinfoil were heated in a strong iron digester to 150°—160° C. After about ten hours' action, the contents of the tubes were transferred to a retort and heated to 120°, to remove all traces of undecomposed iodide of ethyl.

*Action of Zincethyl on Iodide of Stanethyl.*

If the above-mentioned iodide, in a melted state, be added to a quantity of zincethyl in a retort surrounded by cold water, a solid mass is formed, which is again in great part dissolved by agitation and aid of the heat generated. Distillation may be then commenced, and carried on until gases alone come over. The dry residue consists only of chloride of zinc and a little protiodide of tin.

It will not be found economical to saturate the zincethyl at one operation, on account of the caking of the materials, which renders the fracture of the retort very probable; independently of which, the strong heat then necessary partly decomposes the radical when formed. The distillate last obtained should, however, always contain a slight excess of zincethyl; otherwise there is no certainty of removing traces of an iodide, the nature of which will be presently noticed, and which imparts a pungent odour to the radical. By agitation with dilute acid and water, two strata of liquids are produced, the lower of which was fractioned with the thermometer.

At first a little ether appeared, after which the boiling-point ran up quickly to 170°, between which and 180° by far the larger quantity distilled over. The fraction taken between 176° and 180° C. was considered pure, and set apart for examination. It was very combustible, and gave, when ignited, a lurid flame with fine blue edges, and disengaged at the same time a thick cloud of tin oxide.

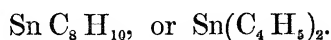
I. 0.2885 grm. of substance gave, when burnt, 0.4265 grm. carbonic acid and 0.2213 grm. water.

II. 0.3117 grm. of substance gave 0.4672 grm. carbonic acid and 0.2455 grm. water.

These numbers correspond to the per-centage composition—

	I.	II.
Carbon . . . .	40.31	40.81
Hydrogen . . . .	8.52	8.72

and also to the formula





The numbers required by theory and obtained by experiment are—

	Theory.		Mean of experiment.
1 equiv. of Tin . .	59	50.43	—
8 equivs. of Carbon .	48	41.02	40.56
10 equivs. of Hydrogen	10	8.55	8.62
	117	100.00	

This radical differs therefore from stannic ethyl, in that it contains double its quantity of ethyl. Accordingly I propose to call it stannic diethyl.

It is a perfectly colourless, limpid, and almost inodorous liquid, very stable, and having a specific gravity of 1.192. It is very insoluble in water, and but slightly so in alcohol. Ether takes it up freely. Cold concentrated acids do not immediately attack stannic diethyl; but when heated, they disengage gases and form salts, which differ in constitution according to the prolongation of the action. Hydrochloric acid converts the substance into an uncrystallizable chloride, insoluble in water, and possessed of an exceedingly pungent and irritating odour. It is only after long digestion that a crystalline body is formed.

With iodine and bromine the action is very violent, and produces hissing as when one drops hot metal into water. Explosion ensues if the two bodies are mixed in any quantity.

An experiment was conducted under water, the bromine being added to the stannic diethyl in such quantity that a slight but permanent red tint showed that it was in excess. An oily liquid was obtained which possessed the characteristic odour, but which, when exposed to the air, shot into a mass of crystals. These were pressed in paper, and placed for some hours under the air-pump before they were analysed.

0.3405 grm. of substance gave 0.3770 grm. bromide of silver, which nearly accords with the number required for bromide of stanethyl,  $\text{Sn C}_4\text{H}_9\text{Br}$ .

	Theory.	Experiment.
Bromine . .	47.07	46.51

The powerful odour of this substance, however, left some reason for doubt as to its exact composition. The salts of stanethyl have been, at different times, stated by FRANKLAND and LÖWIG as odorous and inodorous. Further experiment, therefore, appeared desirable before definitively fixing the formula.

The remaining portion of the bromide was dissolved in weak alcohol, and aqueous potash added. An abundant white precipitate was formed, which, after being well washed, was converted by acid into a chloride. By gentle evaporation, fine hard and almost inodorous crystals were obtained, which differed from the bromide in being easily and entirely soluble in water. The irritating odorous substance was by this treatment entirely transferred to the alkaline solution. This chloride was dried over sulphuric acid and analysed.

0.5070 grm. substance gave 0.3600 grm. carbonic acid and 0.1977 grm. water. This

result places beyond a doubt the composition of the salt, and moreover confirms the last analysis of the bromide.

Chloride of stanethyl,  $\text{Sn C}_4 \text{H}_5 \text{Cl}$ , requires—

	Theory.		Experiment.
1 equiv. of Tin . .	59·0	47·77	—
4 equivs. of Carbon .	24·0	19·43	19·34
5 equivs. of Hydrogen	5·0	4·05	4·32
1 equiv. of Chlorine .	35·5	28·75	—
	123·5	100·00	

It is immaterial whether the bromine be added to the radical, or the radical to the bromine. In both cases the salt of the same radical is formed. If, however, bromine be placed under water, and the vessel be carefully cooled, evolution of gas may be almost entirely prevented. In this case ethyl in its nascent state is presented to free bromine, and bromide of ethyl is produced, which may be readily detected by distillation.

The reaction is in strict accordance with that set forth when describing the mercuric radicals.

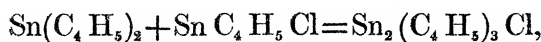
STRECKER has lately shown\*, with much probability, that some of the organo-stannic bodies prepared by LÖWIG may be referred to double salts of comparatively simple formula, the analogues of which may be found in the inorganic oxyiodides and oxychlorides of tin. From the method employed by LÖWIG in forming the stanethyls, viz. by distilling iodide of ethyl with an alloy of tin and sodium disseminated through sand, it may be easily supposed that a partial reduction only of the iodides of stanethyl is effected.

The following experiments prove that various bodies are formed when zincethyl and bichloride of tin react on each other in different proportions, their constitution varying with their more or less complete reduction by the zincethyl. Bichloride of tin produces great heat when dropped into zincethyl. If the tin-salt be in excess, an impure chloride of stanethyl is formed; if the zincethyl be in excess, the radical stannic diethyl is formed; whilst, lastly, if the zincethyl be present in quantity insufficient for the last reaction, that is, less than sufficient to remove the whole of the chlorine, the chief product is an oily body, which possesses the pungent and irritating odour before alluded to. This pungency, which produces continued sneezing, entirely disappears on adding zincethyl to saturation. It is insoluble in water, inflammable, and is clearly a stanethyl chloride. In its chief properties and behaviour it accords with the liquid described by LÖWIG, and named by him "chloride of methylo-stanethyl," the formula of which is  $\text{Sn}_2 \text{C}_{12} \text{H}_{15} \text{Cl}$ .

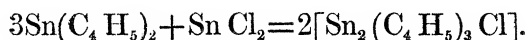
Experiments were then commenced under an impression that the substance in question might prove to be a double compound of stannic diethyl and chloride of stannic ethyl, or, failing that, the liquid might result from a union of three molecules of stannic diethyl with one of bichloride of tin.

\* LIEBIG's Annalen, cv. p. 306.

One of the following expressions, it was thought, might show the synthesis of the chloride:—



or else



To test the first equation, pure inodorous crystals of chloride of stanethyl were added to an excess of stannic diethyl, and kept a short time at the boiling-point. Cold water was then added, and the whole was again raised to ebullition. The aqueous solution was then poured off, and solution of potash added, when an abundant precipitate of oxide of stanethyl showed that no double salt had been effected with the chloride of stanethyl. The portion insoluble in water proved to be the unchanged radical, and did not exhibit the characteristic odour of the oily chloride, which thus could have been readily detected. This negative answer to the first equation showed that the substance was no simple mixture, but a definite compound.

A more satisfactory result was obtained when bichloride of tin was made to act on stannic diethyl, in the proportion of three parts of the former to four parts of the latter. The mixture produced a heat considerably greater than could be borne by the hand, and the liquid partook of a clear brown shade. When exposed to the air it gave slight fumes of vapour, causing much lachrymation.

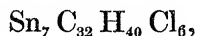
When distilled, ebullition commenced at about  $200^\circ$ ; but no fixed boiling-point could be observed, the thermometer slowly rising up to  $220^\circ$ , at which temperature the whole had volatilized, leaving a mere trace of solid matter in the retort.

The distillate was divided into two portions. That below  $210^\circ\text{C.}$  was of an oily consistence; but above that point the portion solidified, on cooling, into a mass of crystals. These were strongly pressed between bibulous paper, and analysed:—

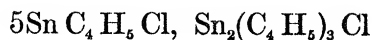
I. 0.4170 grm. of substance gave 0.3440 grm. carbonic acid and 0.1825 grm. water.

II. 0.5138 grm. of substance gave 0.5035 grm. chloride of silver.

These numbers lead most nearly to a formula



which at first seems rather improbable, but which becomes perhaps more intelligible if grouped as a double salt.



requires the following theoretical values:—

	Theory.		Experiment.
7 equivs. of Tin . . .	413	48.15	—
32 equivs. of Carbon .	192	22.37	24.49
40 equivs. of Hydrogen.	40	4.66	4.84
6 equivs. of Chlorine .	213	24.82	24.20
	<u>858</u>	<u>100.00</u>	

Although experiment gives too large a proportion of both carbon and hydrogen for the ascribed formulæ, the salt still less accords with chloride of stanethyl,—from which also the crystals differ, both in form and a sort of fatty consistence.

From the circumstance that no steady boiling-point could be obtained from that portion of the distillate which came over below  $210^{\circ}\text{C}$ ., and which refused to crystallize, it appeared to be no pure chemical compound, but simply a mixture of an oily body and the salt last analysed. This belief was confirmed by noticing its deportment towards aqueous potash, which precipitated a considerable quantity of white oxide of stanethyl. The solution, on the other hand, with hydrochloric acid liberated the above-mentioned odorous oil. To isolate this last, the whole was mixed in a mortar with rather strong aqueous potash, and the magma washed in a funnel plugged with asbestos. The washing was continued with weak potash until the rinsings were nearly inodorous.

The liquid was then distilled, a good condensing apparatus being attached. At first white pungent fumes passed over with the aqueous vapour, and collected in the receiver in the form of oily drops, possessed of great causticity and powerful basic properties. This product, in fact, is the aqueous solution of the oxide of an ethylated base containing tin, from which definite compounds may be obtained with sulphuric, hydrochloric, and other acids.

As the sulphate is but little soluble in water, it seemed well adapted for fixing the constituents of the base. A portion of the aqueous solution of the oxide was therefore nearly neutralized with sulphuric acid, and heated to about  $80^{\circ}\text{C}$ ., when an opaque colourless and crystalline salt appeared, which was dried *in vacuo* over sulphuric acid, and analysed.

I. 0.4661 grm. of substance gave 0.4790 grm. carbonic acid and 0.2470 grm. water.

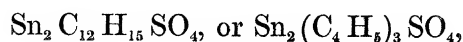
II. 0.5080 grm. of substance gave 0.5223 grm. carbonic acid and 0.2716 grm. water.

III. 0.5529 grm. of substance gave 0.2593 grm. sulphate of barium.

Corresponding to

	I.	II.	III.
Carbon . . . . .	28.01	28.03	—
Hydrogen . . . . .	5.88	5.94	—
Sulphur . . . . .	—	—	6.44

These results point to the formula



which requires

	Theory.		Mean of experiment.
2 equivs. of Tin . . . . .	118	46.64	—
12 equivs. of Carbon . . . . .	72	28.45	28.02
15 equivs. of Hydrogen . . . . .	15	5.92	5.91
1 equiv. of Sulphur . . . . .	16	6.34	6.44
4 equivs. of Oxygen . . . . .	32	12.65	—
	253	100.00	

This substance is identical with the sulphate of LÖWIG'S base, methylo-stanethyl. I would propose a name which has a reference to the true constitution of the salts, and call it sulphate of distanno-triethyl.

This sulphate differs in many respects from the ordinary sulphate of stanethyl. The former is inflammable, and crystallizes either in fine needles or shining grains, which under a low magnifying power present the form of well-defined octahedra. Sulphate of stanethyl, on the other hand, is not combustible, and appears under the microscope in small, somewhat roundish irregular plates. The sulphate of distanno-triethyl, moreover, shows, in a remarkable manner, the unusual character of greater insolubility in hot than in cold water. A clear, cold, saturated solution becomes semisolid when raised to a temperature somewhat short of boiling. The salt is very volatile, and attacks the nose vigorously.

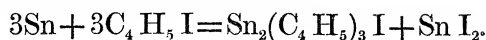
I have not succeeded in isolating the corresponding radical, most probably from the reason that its salts exchange with zincethyl their acid molecule for an additional ethyl atom, and thus are converted into two equivalents of stannic diethyl. Although the affinities of these sesquiethylated compounds are remarkably strong, resisting, as we have seen, the action of potash, there may be some hesitation in assuming with certainty the existence of the radical itself. All the salts may be viewed simply as double compounds; and if future investigation proves them to be such, no exceptional case would arise against viewing them as formed on the type of the tin oxides.

Sesquioxide of tin does not appear to be known either as an artificial or natural product. The bromide and iodide of the sesquiethylated tin base is always one of the products of the action of those elements upon stannic diethyl.

Oxide of distanno-triethyl may be conveniently formed from the sulphate by boiling the salt in strong aqueous potash. If the latter be not in much excess, the oxide is liberated as an oily body, heavier than water, and which solidifies when cold. It is moderately soluble in water, and may be distilled, as has been seen, from aqueous potash. It has a powerful caustic taste, and when left in contact with the skin, produces painful blisters. The aqueous solution precipitates the oxide, on addition of common salt. These properties confirm LÖWIG'S experiments, and very generally accord with the properties of the oxide of methylo-stanethyl.

Occasionally it happens that, from an irregularity in the temperature employed for causing iodide of ethyl to act upon metallic tin, a yellow oily body is formed, and that in sufficient quantity to prevent the crystallization of the iodide of stanethyl. This body has a penetrating odour, and appears to be identical with that obtained by RICHE and CAHOURS. If this impure iodide be treated with aqueous potash, it will be remarked that a comparatively small quantity of oxide of stanethyl falls. The aqueous solution, on the other hand, by distillation yields an alkaline liquid, which furnishes with sulphuric acid a salt with all the properties of sulphate of distanno-triethyl. No doubt therefore remains that the oil is the corresponding iodide of the formula  $\text{Sn}_2(\text{C}_4\text{H}_9)_3\text{I}$ . By separation of biniodide of tin, which is to be found as one of the products of the reaction,

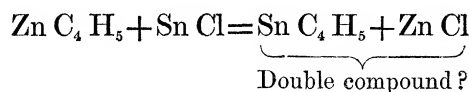
the occurrence of this iodide may be explained,



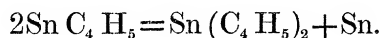
*Action of Zincethyl on Protochloride of Tin.*

To obtain this tin-salt perfectly anhydrous, metallic tin was distilled at a gentle heat with corrosive sublimate. The chloride was powdered, and by little and little introduced into a tube containing zincethyl, which almost immediately became of a yellow colour. After agitating the contents of the tube with anhydrous ether, the solution was pipetted off and allowed to evaporate spontaneously. In this manner a small quantity of stanethyl,  $\text{Sn C}_4\text{H}_5$ , was obtained; but by far the larger quantity remained combined with zincethyl, from which it could not be separated by water, without causing a deposit of metallic tin at the expense of the radical.

Dr. FRANKLAND has before noticed that this radical cannot be distilled without decomposition into tin and a clear liquid. There can be no reasonable doubt of this body being stannic diethyl.

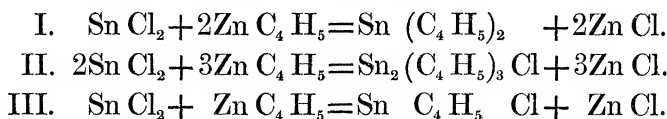


by heat,



This method offers no advantage over that hitherto employed for obtaining the organo-metal, viz. by decomposing the chloride with a strip of zinc.

The several reactions of zincethyl on bichloride of tin may be thus represented, step by step. The tin-salt being added to the zincethyl, we have



It is worthy of remark how prone the metal tin is to assimilate the double equivalent of ethyl, just as we see ordinary oxide of tin passes into binoxide. Salts both of stanethyl and distanno-triethyl readily convert themselves into stannic diethyl.

*Plumbic Diethyl.*

A certain relation has been long recognized between the metals silver, lead, and mercury. This similarity extends to their equivalent weights, the constitution of their salts, and various other characters.

Notwithstanding the sluggish action of iodide of ethyl towards lead, even at high temperatures, there seemed to be no reason to doubt success in preparing the ethylated radical by one of the processes already detailed. LÖWIG has indeed obtained through iodide of ethyl and an alloy of sodium and lead, an iodide analogous to a sesquioxide, in which ethyl plays the part of oxygen. The production of this salt appears to be attended with some difficulty. I have tried LÖWIG's process, but have found the action

of the alloy very slow, even when brought to the boiling-point of iodide of ethyl. Neither bromide nor iodide of ethyl showed any tendency to combine with granulated lead when exposed to a clear April sun for one week, neither did the bodies unite under pressure and a temperature of  $170^{\circ}\text{C}$ . The bromide in the last case was quite unchanged; but the iodide gave crystalline plates of iodide of lead and gaseous matter.

*Action of Zincethyl on Chloride of Lead.*

Chloride of lead turns black immediately it comes in contact with zincethyl. It sinks in the liquid, and forms a crust which is so hard that it will be found more convenient to operate in a bottle than in a retort. In the former vessel the chloride may be incorporated with the zincethyl without fear of fracture.

As soon as the chloride of lead ceases to change colour, the vessel is placed in a water-bath and heated to  $100^{\circ}\text{C}$ ., after which the liquid, when cold, may be decanted. This liquid fumes slightly in the air from the presence of zincethyl, which cannot be wholly saturated even when much chloride of lead is in excess. A compound of the lead radical and zincethyl is thus obtained, which may be treated with very dilute hydrochloric acid and then washed with water. The mass of chloride of zinc in the first bottle may be made to furnish an additional quantity of the radical, by agitation with anhydrous ether.

Considerable difficulty was experienced in freeing this radical entirely from ether. When distilled, the thermometer rises rapidly to nearly  $204^{\circ}$ , at about which point the vapour suddenly decomposes with a slight explosion and deposit of metallic lead.

This difficulty was overcome by conducting the distillation under reduced atmospheric pressure, in a simple condenser a sketch of which is annexed. (See p. 433.)

The apparatus was found very conveniently to permit of frequent change of the receiver, without disturbing the tightness of the various joints. When the barometer stood at 30.5 inches, the radical passed over without the least decomposition at a temperature of  $152^{\circ}\text{C}$ ., under a pressure of about 7.5 inches of mercury, thus depressing the boiling-point in a remarkable degree.

In filling the bulbs for combustion, the precaution was taken of employing the air-pump; and before proceeding to burn the substance, it was found necessary again to empty the bulbs by exhaustion.

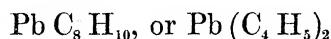
I. 0.3615 grm. of substance gave 0.3928 grm. carbonic acid and 0.2000 grm. water.

II. 0.3116 grm. of substance gave 0.3400 grm. carbonic acid and 0.1775 grm. water.

The composition in 100 parts accordingly is—

	I.	II.
Carbon . . . . .	29.62	29.74
Hydrogen . . . . .	6.14	6.32

the formula,



	Theory.		Mean of experiment.
1 equiv. of Lead . . . .	103·5	64·09	—
8 equivs. of Carbon . . . .	48·0	29·72	29·68
10 equivs. of Hydrogen . . . .	10·0	6·19	6·23
	<hr/> 161·5	<hr/> 100·00	

Plumbic diethyl is a colourless and limped fluid with a faint odour, very like that of the other radicals described. The specific gravity is 1·62. It is soluble in ether, but insoluble in water. It burns brightly, with abundant fumes of oxide of lead. The flame is somewhat differently coloured from that of the tin radical. The latter has an orange flame, with blue edges, whilst the former has a distinct but faint green tinge, with a border less luminous.

It reacts violently on iodine and bromine, so much so as to convert the salts, which doubtless are first formed, into bromide and iodide of lead. When poured into chlorine it bursts, like the tin radical, into flame.

#### *Chloride of Diplumbic Triethyl.*

With concentrated hydrochloric acid the organo-metal yields a crystalline salt with evolution of hydride of ethyl, but by this method it is not easy entirely to convert the radical into chloride.

The chloride is more conveniently formed by passing excess of hydrochloric acid gas into a tube containing plumbic diethyl moistened with aqueous acid. After a brisk effervescence, a solid mass is formed, which may be freely exposed to the air until acid fumes cease to rise. From a solution in ether the crystals may be obtained pure by spontaneous evaporation.

I. 0·6400 grm. of substance gave 0·5088 grm. carbonic acid and 0·2640 grm. water.

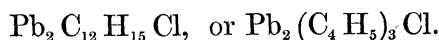
II. 0·7077 grm. of substance gave 0·3240 grm. chloride of silver.

III. 0·5447 grm. of substance gave 0·4985 grm. sulphate of lead.

The calculations for 100 parts, when contrasted with theory, are—

	Theory.		Experiment.
2 equivs. of Lead . . . . .	207·0	62·85	62·51
12 equivs. of Carbon . . . . .	72·0	21·85	21·69
15 equivs. of Hydrogen . . . . .	15·0	4·55	4·57
1 equiv. of Chlorine . . . . .	35·5	10·75	11·32
	<hr/> 329·5	<hr/> 100·00	<hr/> 100·09

This salt accordingly is the chloride of diplumbic triethyl, having the formula



It may be obtained in long colourless crystals, which have a strong penetrating odour, very similar to that of the corresponding body in the tin series. It fuses between watch-



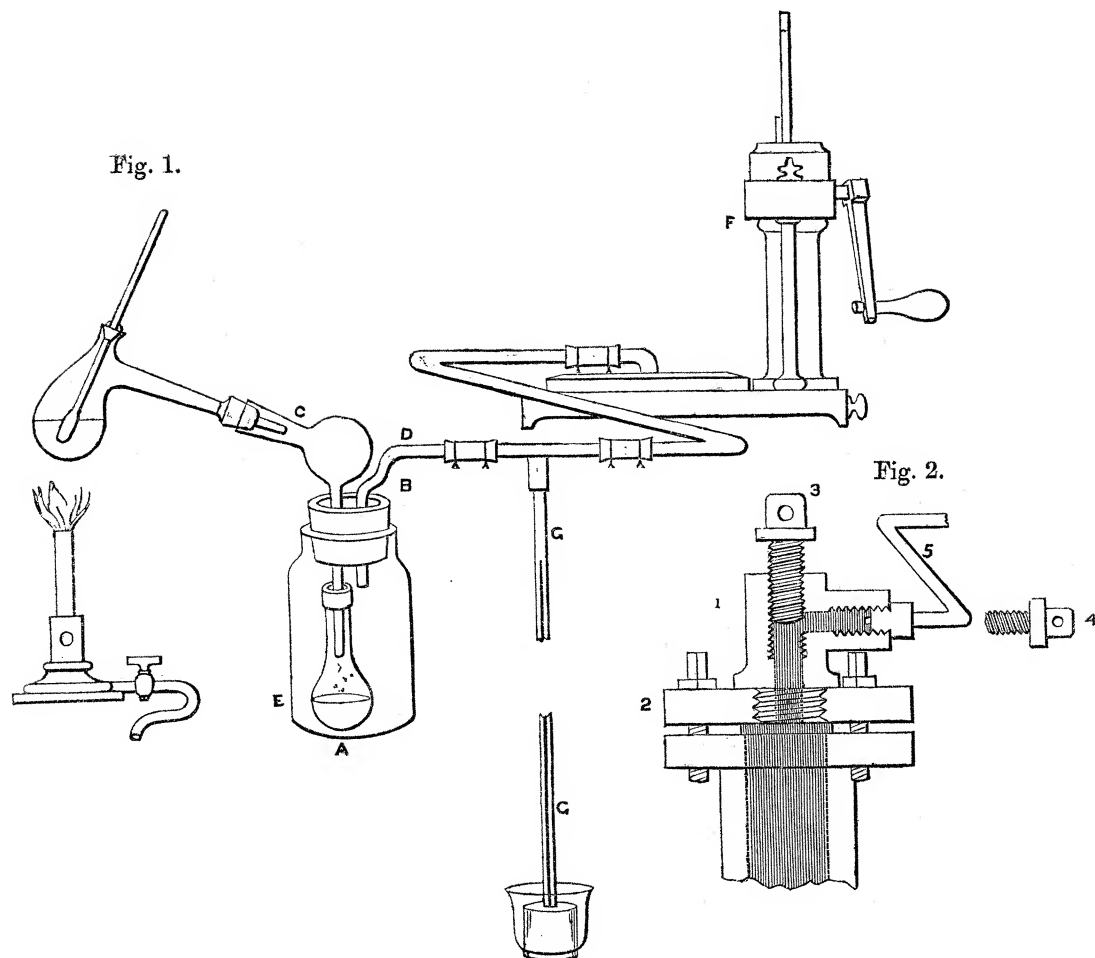


Fig. 1.—Apparatus for distilling Plumbic Diethyl, &c.

- A. A wide-mouthed bottle.
  - B. A well-ground stopper formed from a piece of stout glass tube, 2 inches in diameter. The stopper is ground rather taper to prevent adhesion.
  - C. A small quilled condenser.
  - D. Tube connected by caoutchouc with mercurial gauge.
  - G. Mercurial gauge.
  - F. Air-pump.
- The tubes C and D are cemented into the stopper B by plaster of Paris and a layer of resinous cement to close the pores.
- E. Small receiver capable of being changed when needful.

Fig. 2.—Modification of Dr. FRANKLAND's apparatus for preventing loss by frothing when making zincethyl.

1. Wrought-iron head screwed into upper plate of digester 2; 3, 4 screws with nuts and leaden washers for closing apparatus during the formation of zincethyl.

When distillation is to be performed, the screw 4 is removed and the delivery tube 5 attached. 3 is then partly unscrewed; and if frothing takes place, it passes through 5 into the retort without loss.

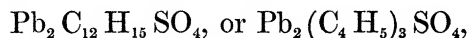
glasses, and ignites at a comparatively low temperature, with the characteristic lead flame.

When heated with concentrated sulphuric acid, the salt blackens, and is converted into sulphate of lead. After addition of a little nitric acid, this carbonaceous deposit is removed, and the sulphate may be used for a quantitative determination of the lead.

*Sulphate of Diplumbic Triethyl*

May be formed by adding dilute sulphuric acid to a warm concentrated solution of the chloride. On account of its greater insolubility, it crystallizes out on cooling, in the form of fine asbestos-like needles. These may be purified by solution in alcohol, in which the sulphate is more soluble than in water. From alcohol the crystals may be obtained of considerable size.

0·5055 grm. of substance gave 0·3850 grm. carbonic acid and 0·2035 grm. water, leading to the formula



which requires the following values:—

	Theory.		Experiment.
2 equivs. of Lead . . . . .	207	60·52	—
12 equivs. of Carbon . . . . .	72	21·05	20·77
15 equivs. of Hydrogen . . . . .	15	4·38	4·47
1 equiv. of Sulphur . . . . .	16	4·64	—
4 equivs. of Oxygen . . . . .	32	9·41	—
	342	100·00	

It would appear, therefore, that from two molecules of the organo-metal, one equivalent of ethyl only is displaced by the negative chlorine, or the compound group  $\text{SO}_4$ . Hitherto my attempts to produce a lead base richer in ethyl have failed. Experiment shows that if chlorine be passed over the sesquiethylated chloride, the decomposition proceeds beyond the removal of the additional equivalent of ethyl; in fact the salt enters into combustion and is entirely destroyed. The aqueous solution of the chloride appears also to be unaffected by a stream of chlorine gas. Chloride of lead is not thrown down.

*Oxide of Diplumbic Triethyl.*

The alkalis do not immediately form precipitates in the aqueous solutions of the salts of this base; but when the solid chloride is gently heated with strong potash, an oily body sinks without liberation of oxide of lead. The same body may be obtained more conveniently through the agency of oxide of silver. The oil which forms on cooling a crystalline mass, is oxide of diplumbic triethyl. It readily volatilizes in white pungent fumes, which provoke sneezing. It strongly blues litmus paper, and attracts carbonic

acid from the air with production of a crystalline salt, which is the carbonate of the base. The various sesquiethylated plumbic salts may be readily obtained from both the oxide and carbonate here described.

Doubtless, from the difficulty hitherto experienced in procuring these plumbic salts, no verification of their properties appears to have been made since the appearance of LÖWIG'S researches above alluded to. On this account, perhaps, less apology may be thought necessary for bringing the foregoing remarks before the attention of the Royal Society.

As a broad field yet remains open for inquiry, I purpose resuming the subject of the organo-metals, but in a somewhat different direction.

*February 28th, 1859.*